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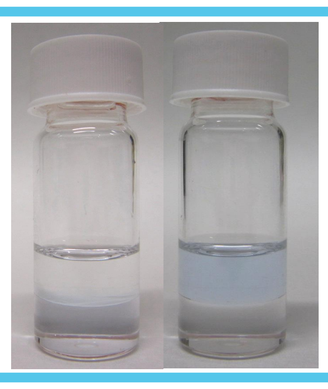
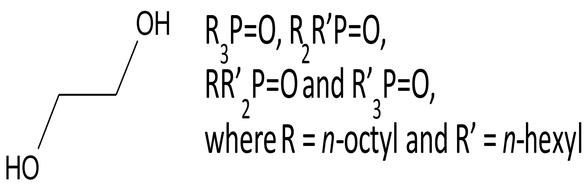
Solvometallurgical separation of rare-earth ions by extraction with two mutually immiscible organic phases

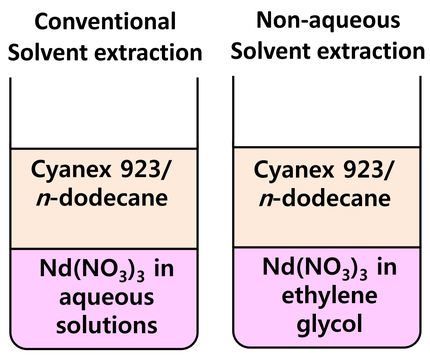
Solvent extraction with two mutually immiscible organic phases is an alternative to conventional solvent extraction with an aqueous feed phase. We developed a solvent extraction process for separation of rare earths, where the more polar organic phase comprises ethylene glycol with dissolved rare-earth nitrate salts and lithium nitrate, while the less polar phase is a solution of the neutral extractant Cyanex® 923 dissolved in *n*-dodecane.



Aim

To prove that the replacement of water in a conventional solvent extraction process by a polar organic solvent can lead to a more selective separation process. This is illustrated for the group separation of heavy rare earth elements (HREEs) from light rare earth elements (LREEs).

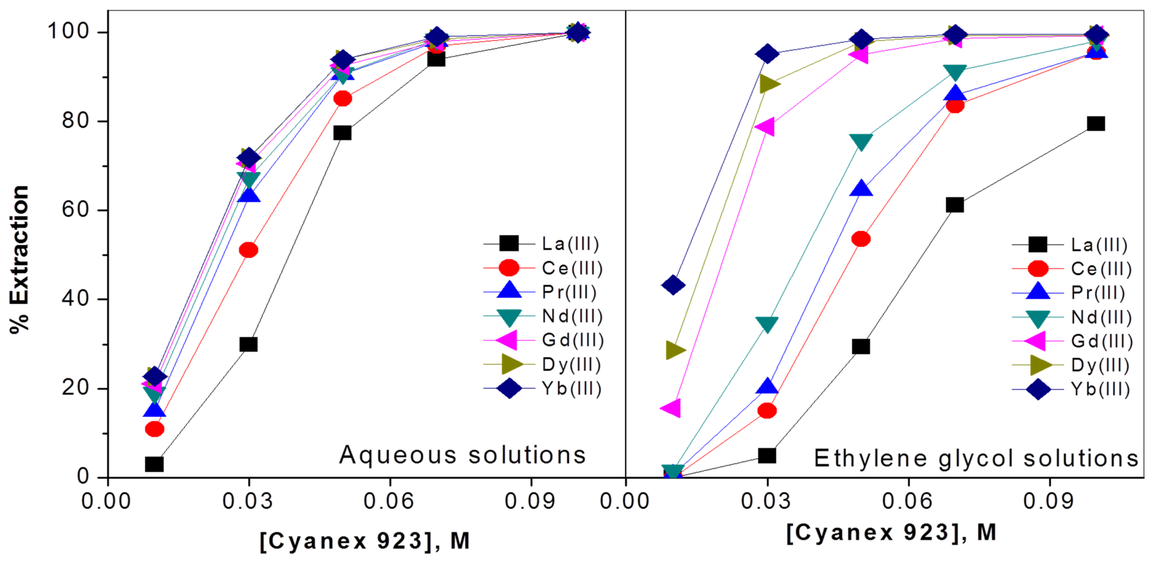




▲ Schematic overview of Conventional and non-aqueous solvent extraction

- Solvent extraction is defined as the preferential distribution of a solute between two immiscible liquid phases.
- Traditionally, water or aqueous solutions are being one of these two liquid phases.
- The replacement of aqueous phase by organic solvents leads to new branch of extractive metallurgy called solvometallurgy.

Influence of Cyanex® 923 concentration



▲ Influence of Cyanex® 923 concentration on the extraction of a mixture of trivalent rare-earth ions from aqueous solutions and non-aqueous ethylene glycol solutions.

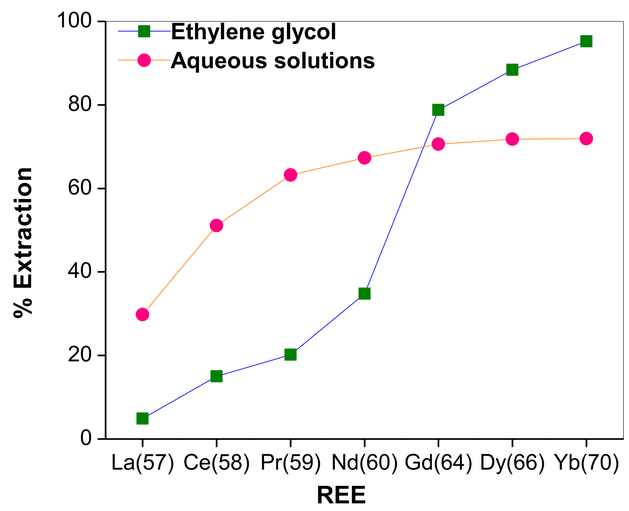
Aqueous solutions

- The %*E* and *D* values for different rare-earth ions are very similar
- separation of mixtures of rare-earth ions is impossible

Ethylene glycol solutions

- The %*E* and *D* values for different rare-earth ions are different
- separation of mixtures of rare-earth ions is possible

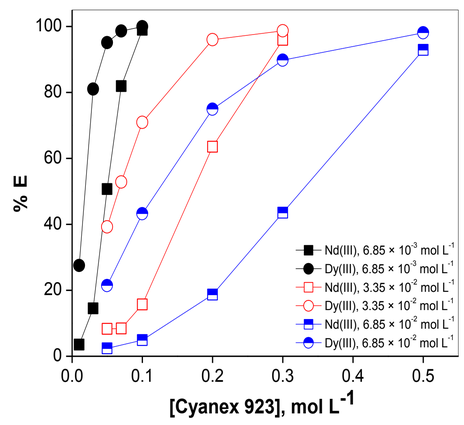
Comparison of extraction from aqueous and non-aqueous solutions



◀ Comparison of extraction behavior for a mixture of trivalent rare-earth ions using 0.03 mol L^{-1} Cyanex® 923. Conditions: [RE(III)] = 1.07 ± 0.2 × 10^{-3} mol L^{-1} (each), [$LiNO_3$] = 1 mol L^{-1}

- The HREEs are more efficiently extracted from ethylene glycol where-as extraction of the LREEs is less efficient compared to aqueous solutions.
- The separation factor of Dy(III) over Nd(III) is 24.6 from ethylene glycol for [Cyanex® 923] = 0.01 mol.L^{-1}, whereas it is only 1.2 from the corresponding aqueous solutions.
- This leads to a better separation of heavy rare earths from light rare earths.
- The separation of Nd(III) and Dy(III) is important for the recycling of rare earths from NdFeB permanent magnets.

Separation of Dy(III) and Nd(III) from ethylene glycol solutions



▲ Influence of the Cyanex® 923 concentration on the binary separation of Nd(III) and Dy(III)

- The maximum separation factors obtained at 3 different concentrations were 25.1, 13.0 and 12.9, respectively.
- separation of binary Nd(III)/Dy(III) mixtures is possible even at industrially relevant concentrations of 10 g L^{-1}

Conclusion

- A new solvent extraction system that is free of aqueous solutions comprising ethylene glycol and dodecane was developed.
- This non-aqueous system can offer advantages over conventional extraction system.
- This extraction system performs better for the group separation of heavy rare earths from light rare earths than the corresponding conventional extraction system with an aqueous phase.